

APPENDIX D

ALTERNATIVE MONITORING PLAN for NSPS Subpart J Refinery Fuel Gas

Conditions for Approval of the Alternative Monitoring Plan for Miscellaneous Refinery Fuel Gas Streams

Refinery fuel gas streams/systems eligible for the Alternative Monitoring Plan (AMP) should be inherently low in H_2S content, and such H_2S content should be relatively stable. The refiner requesting an AMP should provide sufficient information to allow for a determination of appropriateness of the AMP for each gas stream/system requested. Such information should include, but need not be limited to:

- A description of the gas stream/system to be considered including submission of a portion of the appropriate piping diagrams indicating the boundaries of the gas stream/system, and the affected fuel gas combustion device(s) to be considered and an identification of the proposed sampling point for the alternative monitoring;
- A statement that there are no crossover or entry points for sour gas (high H_2S content) to be introduced into the gas stream/system. (This should be shown in the piping diagrams);
- An explanation of the conditions that ensures low amounts of sulfur in the gas stream (i.e., control equipment or product specifications) at all times;
- The supporting test results from sampling the requested gas stream/system using appropriate H_2S monitoring (i.e., detector tube monitoring following the Gas Processor Association's: Test for Hydrogen Sulfide and Carbon Dioxide in Natural Gas Using Length of Stain Tubes, 1986 Revision), at minimum:
 - for frequently operated gas streams/systems - two weeks of daily monitoring (14 samples);
 - for infrequently operated gas streams/systems, 7 samples shall be collected unless other additional information would support reduced sampling.

Note: All samples are grab samples.

- A description of how the two weeks (or seven samples for infrequently operated gas streams/systems) of monitoring results compares to the typical range of H_2S concentration (fuel quality) expected for the gas stream/system going to the affected fuel gas combustion device. (e.g., The two weeks of daily detector tube results for a frequently operated loading rack included the entire range of products loaded out, and, therefore, should be representative of typical operating conditions affecting H_2S content in the gas stream going to the loading rack flare);
- Identification of a representative process parameter that can function as an indicator of a stable and low H_2S concentration for each fuel gas stream/system, (e.g., review of gasoline sulfur content as an indicator of sulfur content in the vapors directed to a loading rack flare);
- Suggested process parameter limit for each stream/system, the rationale for the parameter limit and the schedule for the acquisition and review of the process parameter data. The refiner will collect the proposed process parameter data in conjunction with the testing of the fuel gas stream's stable and low H_2S concentration.

The following shall be used for measuring H₂S in fuel gas within these types of AMPs unless the refiner requests, in writing, for approval of an alternative methodology:

- Conduct H₂S testing using detector tubes ("length-of-stain tube" type measurement);
- Detector tube ranges 0-10/0-100 ppm (N=10/1) shall be used for routine testing; and
- Detector tube ranges 0-500 ppm shall be used for testing if measured concentration exceeds 100 ppm H₂S.

Data Range and Variability Calculation and Acceptance Criteria

For each step of the monitoring schedule, sample range and variability will be determined by calculating the average plus 3 standard deviations for that test data set.

- If the average plus 3 standard deviations for the test data set is less than 81 ppm H₂S, the sample range and variability are acceptable and the refiner can proceed to the next step of the monitoring schedule.

Note: 81 ppm is one-half the maximum allowable fuel gas standard under NSPS Subpart J, and the Agency believes that using 81 ppm acceptance criteria provides a sufficient margin for ensuring that the emission limit is not exceeded under normal operating conditions.

- If the data shows an unacceptable range and variability at any step (the average plus 3 standard deviations is equal to or greater than 81 ppm H₂S), then move to Step 7. Agency approval is required to proceed to the next step if the average plus 3 standard deviations is between 81 ppm and 162 ppm H₂S. As an example, approval may be granted based on a review of the test data and any pertinent information which demonstrates that sample variability during the test period was due to unusual circumstances. Supplemental test data may be taken to demonstrate that process variability is within the plan requirements. Data may be removed from the variability calculations for cause after agency approval.
- For Steps 3 and 4, if the data shows an unacceptable range and variability (the average plus 3 standard deviations is equal to or greater than 81 ppm H₂S), the source will drop back to the previous step's monitoring schedule.
- If at any time, one detector tube sample value is equal to or greater than 81 ppm H₂S, then begin sampling as specified in Step 6. Note: Standard deviation cannot be calculated for a data set containing one point.

Monitoring Schedule for Approved AMPs

For gas streams which must meet product specifications for sulfur content, one time only detection tube sampling along with a certification that the gas stream is subject to product or pipeline specifications is sufficient for the AMP. If the gas stream composition changes (i.e., new gas sources are added), or if the gas stream will no longer be required to meet product or pipeline specifications, then the gas stream must be resubmitted for approval under the AMP.

The following are examples of streams needing one time only monitoring:

- Certified commercial grade natural gas;
- Certified commercial grade LPG;
- Certified commercial grade hydrogen;
- Gasoline vapors from a loading rack that only loads gasoline meeting a product specification for sulfur content.

For other gas streams, the H_2S content of each refinery fuel gas stream/system with an approved AMP shall be monitored per the following schedule:

Step 1:

The refiner will monitor the selected process parameter for each stream/system, according to the established process parameter monitoring or review schedule approved by the agency in the AMP, and at times when conducting H_2S detector tube sampling.

Step 2:

The refiner will conduct random detector tube sampling twice per week for each stream/system for a period of six months (52 samples). For fuel gas streams infrequently generated and combusted in affected fuel gas combustion devices (i.e., less frequent than bi-weekly), detector tube samples shall be taken each time the fuel gas stream is generated and combusted. A total of at least 24 samples shall be collected for infrequently generated gas streams. Monitor and record the selected process parameter in accordance with the established schedule, and at times when conducting H_2S testing. Move to Step 3 if the calculated range and variability of the data meets the established acceptance criteria. Submit test data (raw measurements plus calculated average and variability) to the agency quarterly.

Step 3:

The refiner will conduct random H_2S sampling once per quarter for a period of six quarters (6 samples) with a minimum of 1 month between samples. A minimum of 9 samples are required for infrequently generated and combusted fuel gas streams before proceeding to Step 4. Continue to monitor and record the selected process parameter in accordance with the established schedule, and at times when conducting H_2S testing. Move to Step 4 if the calculated range and variability of the data meets the established acceptance criteria. Submit test data (raw measurements plus calculated average and variability) to the agency quarterly.

Step 4:

The refiner will conduct random H_2S sampling twice per year for a period of two years (4 samples); sample randomly in the 1st and 3rd quarters with a minimum of 3 months between samples. Continue to monitor and record the selected process parameter in accordance with the established schedule, and at times when conducting H_2S testing. Move to Step 5 if the calculated range and variability of the data meets the established criteria. Submit test data (raw measurements plus calculated average and variability) to the agency semiannually.

Step 5:

The refiner will continue to conduct testing on semi-annual basis. Testing is to occur randomly once every semiannual period with a minimum of 3 months between samples. Continue to monitor and record the selected process parameter in accordance with the established schedule, and at times when conducting H₂S testing. If any one sample is equal to or greater than 81 ppm H₂S, then proceed to the sampling specified in Step 7. Note: Standard deviation cannot be calculated for a data set containing one point.

Step 6:

If, at any time, the selected process parameter data indicates a potential change in H₂S concentration, or a single detector tube sample value is equal to or greater than 81 ppm H₂S, then the fuel gas stream shall be sampled with detector tubes on a daily basis for 7 days (or for infrequently generated gas streams - 7 samples during the same period of an indicated change in H₂S concentration, or as otherwise approved by the agency). If the average detector tube result plus 3 standard deviations for those seven samples is less than 81 ppm H₂S, the date and value of change in the selected process parameter indicator and the sample results shall be included in the next quarterly report, and the refiner shall resume monitoring in accordance with the schedule of the current step. If the average plus 3 standard deviations for those seven samples is equal to or greater than 81 ppm H₂S, sampling shall follow the requirements of Step 7.

Step 7:

If sample detector tube data indicates a potential for the emission limit to be exceeded (the average plus 3 standard deviations is equal to or greater than 81 ppm H₂S), as determined in the Data Range and Variability Calculation and Acceptance Criteria or in Step 6, the refiner shall notify the agency of those results before the end of the next business day following the last sample day. The fuel gas stream shall subsequently be tested daily for a two week period (or 14 samples during the same event or as otherwise approved by the agency for infrequently generated gas streams). After the two week period is complete, sampling will continue once per week, until the agency approves a revised sampling schedule or makes a determination to withdraw approval of the gas stream/system from the AMP. Note: At any time, a detector tube value in excess of the 162 ppm limit is evidence that the emission standard has been exceeded.

General Provisions of Approved AMPs

Upon agency request, the refiner shall conduct a test audit for any gas stream with an approved AMP. The audit shall consist of daily detector tube samples collected over a one week period (7 samples). For fuel gas streams infrequently generated and combusted in affected fuel gas combustion devices, an audit shall consist of 3 consecutive sampling events. (e.g., Rail loading may occur once per month, an audit would consist of 3 consecutive loading events.) The United States Environmental Protection Agency, with due notice, reserves the right to withdraw approval of the AMP for any gas stream/system.

The source shall keep records of the H₂S detector tube test data and the representative process parameter data and fuel source for at least two years.

If a new fuel gas stream is introduced into a fuel gas stream with an approved AMP, the refiner shall again apply for an AMP and repeat Steps 1 - 5.

Example:

An AMP Application for a Hydrogen Plant PSA Off-Gas Stream Combusted Exclusively in the Hydrogen Plant Process Heater:

Process Description

Hydrogen production for the refinery by the steam methane reforming process. CO_2 is the primary impurity in the hydrogen produced; small amounts of CO and methane are also present. Unpurified hydrogen is passed over molecular sieve absorbent beds to remove these impurities. The off gas from regeneration of the absorbent beds is called PSA off-gas. It is sent to the hydrogen plant heater to recover heat and control CO emissions.

Piping Diagrams

Piping diagrams should be supplied to show monitoring location and to demonstrate that there is no potential for cross over or entry points for sour gas.

Basis for PSA Off-Gas Low H_2S Content

Since PSA off-gas is a byproduct of hydrogen purification, any H_2S in the PSA purge gas must come from the hydrogen unit feed. Levels of H_2S in the PSA gas are negligible because H_2S must be controlled to prevent deactivation of the unit's catalyst

H_2S is a permanent catalyst poison. The hydrogen unit has 2 scrubbers to remove H_2S from the feed gas to protect the unit's catalyst from H_2S poisoning. The scrubbers are operated in series. The lead scrubber must exhibit at least a 70% reduction in H_2S content. If not, the scrubber is taken off line and the absorbent is replaced. After the absorbent is replaced, the scrubber is placed on line as the second scrubber in series. This maximizes the amount of H_2S removal and assures maximum scrubbing potential when one scrubber is off line for absorbent replacement.

Process Parameter Monitoring and Suggested Process Parameter Limit

Operation of the scrubbers is checked on a monthly basis with detector tubes. The feed gas H_2S content is measured at the inlet and outlet of the lead scrubber. If natural gas is used as hydrogen plant feed; both readings are below the 1 ppm detection limit. If refinery fuel gas is the feed gas, 30 ppm to 40 ppm H_2S is normally detected at the inlet. A lead scrubber outlet reading of 10 -12 ppm H_2S would trigger absorbent replacement. The suggested process parameter limit is 20 ppm H_2S at the lead H_2S absorber outlet. Absorber outlet H_2S measurements will be taken in conjunction with the PSA gas measurements during Steps 2 and 3.